

AD-A137 988

PROPERTIES OF POLYURETHANE ANIONOMERS: IONIZATION VIA
BIMOLECULAR NUCLEOP. (U) WISCONSIN UNIV-MADISON DEPT OF
CHEMICAL ENGINEERING K K HWANG ETAL. 01 FEB 84 TR-2
N00014-83-K-0423

1/1

UNCLASSIFIED

F/G 11/9

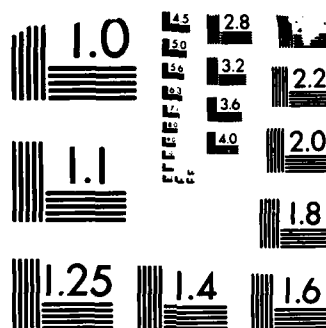
NL

END

FILED

6 54

DEC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER 2		2. GOVT ACCESSION NO. 4D A137988	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PROPERTIES OF POLYURETHANE ANIONOMERS: IONIZATION VIA BIMOLECULAR NUCLEOPHILIC DISPLACEMENT OF THE URETHANE HYDROGEN		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report	
7. AUTHOR(s) K. K. S. Hwang, T. A. Speckhard and S. L. Cooper		6. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0423	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemical Engineering University of Wisconsin Madison, WI 53706		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS --	
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE February 1, 1984	
		13. NUMBER OF PAGES 32	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION, DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Distribution unlimited			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES To be published in Journal of Macromolecular Science-Physics			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polyurethane, anionomer, structure-property study, block copolymer gamma			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two series of polyether polyurethane anionomers based on 4,4' diphenylmethane diisocyanate (MDI) and polytetramethylene oxide (PTMO) were synthesized and their properties investigated. Ionization proceeded via a bimolecular nucleophilic displacement reaction with sodium hydride followed by a ring opening reaction with γ -propane sultone. The lower hard segment content (20 wt% MDI) control material exhibited an initial one phase morphology that underwent phase separation upon ionization with subsequent development of hard segment ordering. These changes in morphology were accompanied by dramatic improvements in			

DTIC
ELECTE
FEB 17 1984
S
E

DTIC FILE COPY

DD FORM 1473

EDITION OF 1 NOV 65 IS OBSOLETE

S N 0102-LF-01J-6601

(cont.)


SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

84 02 046

AD A137988

20. Abstract (cont.)

Mechanical properties. The 38 wt% MDI control material possessed a two phase morphology and well developed hard segment ordering. Ionization disrupted the hard segment ordering and at low levels decreased the degree of phase separation. Further ionization led to reattainment of the original degree of phase separation and a marked improvement in mechanical strength. The differences in properties of the two series of materials are discussed and compared with properties of other polyurethane ionomers reported in the literature.



OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0423

TECHNICAL REPORT NO. 2

Properties of Polyurethane Anionomers:
Ionization via Bimolecular Nucleophilic
Displacement for the Urethane Hydrogen

by

K. K. S. Hwang, T. A. Speckhard, and S. L. Cooper

Prepared for Publication

in the

Journal of Macromolecular Science-Physics

Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin 53706

February 1, 1984

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited



INTRODUCTION

The incorporation of ionic functionality into the hard segment units of polyurethane block copolymers produces materials known as polyurethane ionomers which possess improved mechanical properties (1-6). The improvement of properties has been attributed to changes in morphology and microstructure upon ionization. Ionization increases the polarity difference between the hard and soft segments and thus has been found to improve the degree of phase separation. Ionization also improves hard segment domain cohesion through coulombic interactions of the ionic groups. Both of these effects enhance the ability of the hard segment domains to act as a filler and a physical crosslink thereby increasing the strength of the material. For a more thorough introduction to this subject the reader is referred to the introduction in the preceeding paper.

In previous studies of polyurethane ionomers (1-6), data has been presented on materials that incorporate N-methyl diethanolamine (MDEA) as the hard segment chain extender. Ionization proceeds by quarternization of the tertiary amine of MDEA followed by reaction in solution with γ -propane sultone. A ring opening reaction occurs on the sultone resulting in the formation of a quarternary ammonium ion closely linked to a sulfonyl anion. The material produced is termed a zwitterionomer (1,6). The zwitterionomer can be further reacted to produce materials known as cationomers or anionomers. Anionomers are produced via reaction of the zwitterionomer with a metal acetate producing a metal-sulfonyl ion pair with reduction of the ammonium ion to the tertiary amine by generation of methyl acetate (3). In this case the charge on the polymer backbone is negative and thus the material is termed an anionomer. A positively charged polymer backbone results when the MDEA extended polyurethane is reacted with an alkyl halide to produce a quarternary ammonium halide pair - a cationomer. The limitation of these synthetic schemes is that the hard segment chain extender must contain a tertiary amine group.

An alternate method of producing polyurethane anionomers involves the bimolecular nucleophilic displacement reaction of the urethane hydrogen (4,5). The advantage of this method is that it is not dependent on the choice of chain extender and can thus be carried out on a wide variety of polyurethane block copolymers. Another difference compared with the method based on MDEA is that the potential maximum ionic content is higher since there are more ionization sites per hard segment unit. For example, in a 3/2/1 molar ratio diisocyanate/MDEA/soft segment material there are three urethane hydrogens for every tertiary amine group. The basic synthetic procedure is shown in scheme 1. The urethane nitrogen is first reduced by reaction with sodium hydride in N,N-dimethylformamide (DMF) solution producing hydrogen gas. The nitrogen anion is then reacted with γ -propane sultone which undergoes a ring opening reaction to produce the polyurethane anionomer.

Using the method outlined above, two series of polyether polyurethane anionomers were prepared (Table 1) from conventional polyether polyurethanes PTMO-20 (ET-20) and PTMO-38 (ET-38). PTMO-20 is a 1:1 copolymer of 4,4' diphenylmethane diisocyanate (MDI) and polytetramethylene oxide (PTMO) (number average molecular weight of 1000) exhibiting a one phase morphology (1). This polymer contains 20 wt% MDI. It should be noted that recent work has apparently shown that PTMO-20 (ET-20) can with aging develop a phase separated morphology (7,8). PTMO-38 is synthesized from a 3/2/1 molar ratio of MDI/butane diol (BD)/PTMO (1000). PTMO-38 contains 38 wt% MDI and possesses a phase separated morphology (9). Each of these polymers was subsequently ionized to several different levels (Table 1). The nomenclature used in Table 1, for example PTMO-20-4.5, describes the soft segment type (PTMO), weight percent MDI (20), and the weight percent NaSO_3 (4.5).

The purpose of this investigation was to study the effects of ion incor-

poration and ionization level on the morphology and properties of PTMO based polyurethane block copolymers. The polyether polyurethane anionomers described above were investigated using differential scanning calorimetry (DSC), infrared spectroscopy (IR), dynamic mechanical analysis and stress-strain testing techniques. The results of this study are compared with results on other anionomers (3) and zwitterionomers (1) that were synthesized from polyurethanes containing MDI, 1000 molecular weight PTMO and MDEA.

EXPERIMENTAL

Materials

4,4' diphenylmethane diisocyanate (MDI, Eastman Kodak Chemical Co.) and γ -propane sultone (Aldrich Chemical Co.) were vacuum distilled. Polytetramethylene oxide (PTMO, Quaker Oats Co.) was dehydrated under vacuum at 50°C for two days. 1,4 butane diol (BD, Aldrich) was dehydrated over calcium hydride for two days and then vacuum distilled. N,N-dimethyl formamide (DMF, Aldrich) was degassed for 48 hours. Sodium hydride (NaH, Aldrich) and stannous octoate (M&T Chemicals) were used as received.

Synthesis

1. Polyurethane Block Copolymers

PTMO based polyurethane block copolymers were synthesized by a bulk condensation polymerization technique in a nitrogen atmosphere. PTMO-20, the MDI/PTMO copolymer, was prepared by mixing PTMO and molten MDI in a one to one molar ratio along with .15 wt% stannous octoate catalyst. To ensure complete reaction the mixture was kept at 100°C for ten hours. PTMO-38 was prepared by the conventional two step melt polymerization procedure (10). A three to one molar ratio of MDI and PTMO and .15 wt% catalyst was first mixed to generate the MDI tipped PTMO oligomers. Chain extension was accomplished by adding the appropriate amount of BD to produce an overall 3/2/1 molar ratio of MDI/BD/PTMO. To ensure that the reaction was complete the reaction mixture was kept at 100°C

for ten hours.

2. Polyurethane Anionomers

Polyurethane anionomers were synthesized according to scheme 1. The polyurethane block copolymer was dissolved in DMF (5 % wt/vol) and mixed with a dispersion of NaH in DMF. The reaction mixture was kept at -5 to 0°C under nitrogen and vigorously stirred. Within approximately seven minutes a greenish-yellow color appeared. After stirring for 15 minutes an equivalent amount (compared with NaH) of γ -propane sultone was added and the mixture was kept at 50°C for 1 hour. The nitrogen substitution reaction was confirmed by infrared spectroscopy and nuclear magnetic resonance experiments. No observable change in molecular weight of the polyurethane ($M_w = 60,000$ using a polystyrene calibration scale) due to the NaH reaction was observed in gel permeation chromatography experiments using the method described by Adibi et al (11). Adibi et al. used methyl iodide to methylize the sodium substituted polyurethane and found that the molecular weight of the methylized polyurethane was the same as the molecular weight of the original material provided that the NaH reaction was carried out at 0°C.

The reaction solution was filtered and precipitated into toluene. The precipitated anionomer was further washed with refluxing methanol in a soxhlet extractor for at least three days to remove any residual γ -propane sultone and NaH. Elemental analysis for sodium indicated that the NaH reacted completely. Finally, the materials were dried under vacuum at 50°C for one week. It should be noted that the higher ionic content samples tended to absorb water upon exposure to atmosphere. In fact higher ionic content PTMO-38 based materials than those shown in Table 1 were prepared but these materials absorbed significant amounts of water upon exposure to the atmosphere and became quite soft. Also, after exposure to the atmosphere these highly ionized materials were insoluble in N,N-dimethyl acetamide (DMA) unlike the materials listed in Table 1.

Samples for mechanical and thermal testing were prepared by compression molding at 180°C for three minutes followed by slow cooling to room temperature. The cooling process took approximately four hours. Samples for infrared spectroscopy experiments were prepared by spin casting from dilute DMA solutions.

Characterization

Differential scanning calorimetry (DSC) thermograms were recorded from -150 to 230°C using a Perkin-Elmer DSC 2 equipped with a data processing unit. The heating rate was 20°C/minute and the quenching rate was 320°C/minute. The data processing unit allowed automatic subtraction of the background and normalization of the thermograms for sample weight.

Dynamic mechanical data were obtained using a microprocessor controlled Rheovibron DDV-II. Samples were cooled to -150°C and data were taken at a test frequency of 110 Hz and a temperature rise rate of 1°C/minute.

Room temperature uniaxial stress-strain data were taken on an Instron table model tensile testing device at a crosshead speed of .5 in/min. Samples were prepared using an ASTM D412-D standard die.

Infrared survey spectra were recorded using a Perkin-Elmer 180 double beam spectrophotometer.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Figure 1 shows IR survey spectra for both polyether polyurethane control materials and two of the corresponding high ionic content anionomers. In both control polymers the NH band in the region of 3200-3500 cm^{-1} appears almost completely hydrogen bonded since the NH bonded peak at 3310 cm^{-1} predominates while the free (non-hydrogen bonded) NH peak at 3460 cm^{-1} is barely detectable. However the carbonyl band in the region of 1650-1750 cm^{-1} is significantly dif-

ferent in the two control materials. For PTMO-20 the carbonyl absorption is predominantly found at 1730 cm^{-1} representing non-bonded carbonyl groups with a shoulder at 1700 cm^{-1} due to hydrogen bonded carbonyls. Since the NH group is mostly hydrogen bonded while the carbonyl group is not, it appears that the NH groups are bonded to other hydrogen bond acceptors in the materials - presumably the soft segment ether groups (12). A large amount of hydrogen bonding between the urethane and ether groups is suggestive of a one phase morphology with hard segments dispersed in a soft segment matrix. In contrast, the IR spectra of PTMO-38 indicates a majority of both the urethane and carbonyl groups are hydrogen bonded. This behavior is typical of a phase separated polyurethane where the hydrogen bonding occurs mainly in the hard segment domains (12).

Ion incorporation has a profound effect on the hydrogen bonding characteristics of the polyether polyurethanes. A comparison between the spectra of PTMO-20 and PTMO-20-10.3 reveals that upon ionization the carbonyl absorption changes from primarily free to primarily bonded. This would indicate aggregation of hard segments since the soft segments do not contain any electron acceptors. In addition, since in sample PTMO-20-10.3 70% of the urethane hydrogens are replaced (Table 1), the data suggest interactions between carbonyl groups and sodium atoms. Ionization also decreases the bonded nitrogen absorption as expected since 70% of the urethane hydrogens are replaced. The small peak at approximately 3575 cm^{-1} could be due to free NH groups but is more likely OH bonding resulting from a small amount of absorbed water.

Ionization of PTMO-38 to PTMO-38-6.5 produces different effects. In this case, ion incorporation is accompanied by a decrease in the bonded carbonyl fraction. Also, the NH peak is broadened, shifted to a slightly lower wavenumber, and its area is decreased. The change from bonded to free carbonyl groups would seem to indicate an unexpected decrease in the degree of phase separation. A similar phenomena has been observed previously for zwit-

terionomers and attributed to urethane groups bonding to the stronger proton accepting sulfonyl groups (2). This explanation is also suggested by a shift of the bonded NH peak to lower frequencies indicating participation in a stronger hydrogen bond. However, as discussed above this behavior was not observed for the PTMO-20 materials. PTMO-38 is an MDI/BD based polyurethane known to contain a microphase separated morphology in which ordered urethane domains possess a high degree of interurethane hydrogen bonding (13). Thus it is also possible that the change in carbonyl behavior is at least partially due to disruption of the ordered packing arrangement upon ionization. That is, ionization of the hard segments may impede formation of ordered structures by reducing the symmetry of the hard segment units and increasing steric hindrance. Disruption of packing is also suggested by the appearance of a free NH shoulder in the NH absorption peak of sample PTMO-38-6.5. The differences in the hydrogen bonding behavior of the two ionized samples are apparently a result of different domain structures resulting from the differences in hard segment length and ionic content.

Thermal Analysis

DSC curves are shown in Figures 2 and 3 for the PTMO-20 and PTMO-38 series materials respectively. Thermal transition data are summarized in Tables 2 and 3 respectively. For each material a compression molded sample (control) was heated at 20°C/min up to 230°C and then quench cooled and heated again. The results for the PTMO-20 series materials show a dramatic change in thermal behavior with increasing ionic content. The unionized PTMO-20 sample exhibited a sharp glass transition zone unaffected by quenching, characteristic of a one phase material. The glass transition of PTMO-20-0.8 is centered at a slightly lower temperature and the heat capacity change (ΔC_p) is smaller (Table 2) indicating that some phase separation is beginning to occur. Further increasing of the ionic content to 4.5% results in a noticeably broader glass transition cen-

tered at a lower temperature with a smaller ΔC_p . All of these results can be attributed to the development of phase separation. More interesting however is the development of some ordering in the hard segment domains that leads to the distinct endotherm observed at 105-110°C. This ordering and phase separation closely parallels the change from mostly free to mostly bonded carbonyl groups in the IR spectra. Further, increases in ionic content (samples PTMO-20-10.3 and PTMO-20-12.1) continue to lower the soft segment glass transition temperature and narrow the transition zone indicating increasing phase separation. The decreased ΔC_p also observed with increasing ionization implies an increase in the degree of physical crosslinking which restrains soft segment mobility. Increasing ionic content also improves hard segment domain cohesion as indicated by the hard segment ordering endotherm moving to higher temperatures.

The results of increasing ionic content on the PTMO-38 series materials are noticeably different as might be expected based on the infrared analysis. The unionized PTMO-38 exhibits thermal behavior characteristic of phase separated MDI/BD based polyurethanes. The three high temperature endotherms have been attributed to various degrees of ordering in the hard segment domains (14). When PTMO-38 is quenched from high temperature a more phased mixed state relative to the initial state is 'frozen in' resulting in a higher soft phase glass transition temperature. After passing through the glass transition a large exothermic peak and two endotherms are observed. This is probably due to recrystallization of the hard segments which is followed by a disordering and melting endotherm (15,16).

Low degrees of ionization in PTMO-38 results in materials (PTMO-38-1.3, PTMO-38-3.3) with a higher soft segment glass transition indicating a decrease in the degree of phase separation. As suggested by the IR analysis this unusual behavior is probably due to disruption of hard segment ordering. The well defined endotherms observed for PTMO-38 are not present in PTMO-38-1.3 and

PTMO-38-3.3. Apparently ionization disrupts favorable hard segment packing arrangements causing more hard segments to be dispersed in the soft phase. Further ionization to 6.5% produces a material (PTMO-38-6.5) with the same soft segment glass transition temperature as the original material (PTMO-38); it appears that the effect of increasing segmental polarity difference is offsetting the effect of disrupting the hard segment ordering. Since a well defined high temperature endotherm is not observed it is unlikely that the increase in the degree of phase separation is a result of increasing ionization creating new favorable packing arrangements.

The existence of well defined hard segment endotherms in the phase separated PTMO-20 based materials is interesting because similar endotherms have not been reported previously for polyurethane ionomers. This is due to the fact that previously studied polyurethane ionomers were based on MDEA extended hard segments. MDEA is an asymmetric molecule and its incorporation in the hard segment tends to disrupt hard segment ordering. However, it is also interesting that similar distinct endotherms are not observed for the PTMO-38 based anionomers. This is likely a result of the longer hard segment length and broader hard segment length distribution of PTMO-38. The PTMO-20 based materials only contain one MDI unit long hard segments which should therefore pack easily. In contrast, the PTMO-38 materials probably contain a wide distribution of hard segment lengths (8,17).

Dynamic Mechanical Analysis

The results of dynamic mechanical experiments are displayed in Figures 4 and 5 for the PTMO-20 and PTMO-38 series materials respectively and parameters determined from the curves are summarized in Table 4. Figure 4 shows that the storage modulus of PTMO-20 does not exhibit a plateau region following the glass transition. This agrees with the DSC and IR results since it indicates that PTMO-20 is a one phase material. Upon ionization a plateau region develops and

the plateau modulus rises with increasing ionization level. This indicates increasing phase separation and an enhancement of the physical crosslinking and filler effects. The dramatic extension of the plateau region to higher temperature with increasing ionization is indicative of greatly enhanced hard segment domain cohesion. Both of these results are in agreement with the DSC data. Using the position of the E'' peak (β max, Table 4) as a measure of the position of the soft phase glass transition temperature reveals the trend noted previously of decreasing glass transition with increasing ionization attributed to increasing phase separation. Ionization also results in a small secondary maximum (β' max, Table 4) in the loss modulus curve indicating some disruptive process in the hard segment domains. This maximum moves to higher temperatures with increasing ionic content demonstrating improved domain cohesion.

The dynamic mechanical behavior of the PTMO-38 series materials is shown in Figure 5. Once again there is agreement with the DSC results. The position of the β max peak in the E'' curve can be seen to exhibit the same trend with ionic content as the glass transition temperature measured by DSC. A slight increase in the plateau modulus between 0 and 100°C in the PTMO-38-1.3 and PTMO-38-3.3 samples relative to PTMO-38 can be primarily attributed to an increase in the glass transition temperature which effectively shifts the E' curves to higher temperatures. Sample PTMO-38-6.5 however exhibits a marked modulus enhancement. This could be related to a change in morphology or hard segment domain structure but based on the DSC analysis is probably simply the result of regaining a high degree of phase separation coupled with enhanced domain cohesion due to the high ionic content. The high temperature transition (shoulder) (β' max, Table 4) in the E'' curve of the ionized samples is probably a hard segment glass transition that is not observed in the more ordered PTMO-38 control sample. Heating past this glass transition eliminates the dimensional stability provided by the hard

segment domains and causes as expected a sudden drop in the storage modulus that effectively limits the high temperature use of these materials.

Tensile Properties

Stress-strain curves are presented in Figures 6 and 7 for the PTMO-20 and PTMO-38 based materials respectively. Tensile properties are summarized in Table 5. The unionized PTMO-20 sample is too soft and weak to be tested at room temperature. Figure 6 and Table 5 show that the strength and extensibility of this material is remarkably improved even at low levels of ionic content. Based on the previous experiments, the increase in tensile properties upon ionization is attributed to the development of a two phase morphology. At high levels of ionization, the materials behave more like a plastic, exhibiting a high modulus and a low elongation at break.

The PTMO-38 control material exhibits the tensile properties of a good conventional elastomer. Initially ionization does not improve the modulus, a result that agrees with the dynamic mechanical data. Low degrees of ionization do give rise to higher stresses at break with correspondingly lower elongations. At higher ionic content (sample PTMO-38-6.5), a much higher modulus in accord with the dynamic mechanical data is observed. The tensile properties of sample PTMO-38-6.5 are roughly comparable with tensile properties of MDEA based zwitterionomers of similar chemistry and ionic content and are better than tensile properties reported for MDEA based anionomers (1,3).

Summary

Two series of polyether polyurethane anionomers have been synthesized and their properties investigated using DSC, IR, stress-strain and dynamic mechanical analysis. PTMO-20 exhibited a one phase morphology that upon ionization underwent phase separation. Further ionization improved the degree of phase separation and hard segment domain cohesion. Higher ionic content samples also

exhibited a distinct high temperature endotherm indicative of hard segment ordering. As a result of these morphological changes, increasing ionic content led to a greater dynamic modulus that was extended to much higher temperatures, and improved tensile properties.

In contrast, the PTMO-38 material demonstrated a two phase morphology and a high degree of hard segment ordering. Low levels of ionization disrupted this hard segment ordering thereby decreasing the degree of phase separation, but it did not appreciably affect the mechanical properties. As the ionic content was increased a high degree of phase separation was reattained resulting in a dramatic improvement in the mechanical properties. However, there was still no evidence of hard segment ordering. The lack of ordering in these materials was attributed to the broad hard segment length distribution of PTMO-38 in contrast to the monodisperse one unit long hard segments of PTMO-20 which should pack more readily.

ACKNOWLEDGEMENTS

The authors would like to acknowledge partial support of this work by the Polymers Section of the Division of Materials Research of the National Science Foundation through grant DMR-81-06888 and by the Office of Naval Research and Naval Air Systems Command through contract N00014-83-0423.

References

1. K. K. S. Hwang, C. Z. Yang, and S. L. Cooper, Poly. Engr. & Sci., 21, 1027 (1981).
2. C. Z. Yang, K. K. S. Hwang, and S. L. Cooper, Makromol. Chem., 184, 651 (1983).
3. J. A. Miller, K. K. S. Hwang, and S. L. Cooper, J. Macromol. Sci.-Phys. B22, 321 (1983).
4. J. A. Miller, K. K. S. Hwang, C. Z. Yang, and S. L. Cooper, J. Elast. and Plas., 15, 174 (1983).
5. D. Dieterich, W. Keberle, and H. Witt, Angew. Chem. Intern. Ed., 9, 40 (1970).
6. T. A. Speckhard, K. K. S. Hwang, C. Z. Yang, W. R. Laupan, and S. L. Cooper, accompanying paper
7. K. K. S. Hwang, unpublished results.
8. S. B. Lin, K. K. S. Hwang, K. S. Wu, P. E. Gibson, and S. L. Cooper, submitted to Macromolecules.
9. D. S. Huh and S. L. Cooper, Polym. Engr. and Sci., 11, 369 (1971).
10. J. H. Saunders and K. C. Frisch, "Polyurethane Chemistry and Technology, Part I. Chemistry", Interscience, New York (1962).
11. K. Adibi, M. H. George, and J. A. Barrie, Polymer, 20, 483 (1979).
12. V. W. Srichatrapimuk and S. L. Cooper, J. Macromol. Sci.-Phys., B15, 207 (1978).
13. R. Bonart, L. Morbitzer, and E. H. Muller, J. Macromol. Sci.-Phys., B9, 447 (1974).
14. R. W. Seymour and S. L. Cooper, Macromolecules, 6, 48 (1973).
15. C. M. Brunette and W. J. Macknight, Rubber Chem. and Tech., 55, 1428 (1981).
16. M. F. Froix and J. M. Pochan, J. Polym. Sci.-Phys., 14, 1047 (1976).
17. L. L. Harrell, Jr., Macromolecules, 2, 607 (1969).

Table I

Sample	Composition			Wt% Hard Segment	% of Urethane Hydrogens Replaced ^a	Wt% NaSO ₃	
	MDI	BD	PTMO			Calculated ^b	Exp ^c
PTMO-20	1	0	1	20	-	0	-
PTMO-20-8	1	0	1	20	5	.8	.8
PTMO-20-4.5	1	0	1	20	29	4.5	4.5
PTMO-20-10.3	1	0	1	20	70	10.3	10.3
PTMO-20-12.1	1	0	1	20	85	12.1	12.1
PTMO-38	3	2	1	48	-	0	-
PTMO-38-1.3	3	2	1	48	4	1.3	-
PTMO-38-3.3	3	2	1	48	11	3.3	-
PTMO-38-6.5	3	2	1	48	22	6.5	-

^a Calculated based on amount of Na and MDI added during synthesis.

^b Calculated based on amount of Na and SO₃ added during synthesis.

^c Calculated based on wt% Na measured by Galbraith Laboratories Inc.
Values based on wt% S were slightly higher.

Table II
Differential Scanning Calorimetry Data

Sample	Glass Transition			T _m (°C)
	T _g (°C) ^A	Breadth (°C)	$\Delta C_p \frac{\text{mCal}}{\text{g}^\circ\text{C}}$	
PTMO-20-0(C)*	-55	16	144	-
PTMO-20-0(Q)*	-55	16	144	-
PTMO-20-8(C)	-57	17	129	-
PTMO-20-8(Q)	-57	17	129	-
PTMO-20-4.5(C)	-62	26	123	107
PTMO-20-4.5(Q)	-62	27	120	106
PTMO-20-10.3(C)	-68	22	117	146
PTMO-20-10.3(Q)	-65	24	105	153
PTMO-20-12.1(C)	-73	18	108	197
PTMO-20-12.1(Q)	-70	20	90	202

^A Midpoint (1/2 ΔC_p)

* C = Control
Q = Quench

Table III
Differential Scanning Calorimetry Data

Sample	NaSO ₃	Glass Transition		
		T _g (°C) ^A	Breadth	$\Delta C_p \frac{mCal}{g^\circ C}$
PTMO-38 (C)*	0	-44	34	99
(Q)*	0	-12	34	144
PTMO-38-1.3 (C)	1.3	-31	47	66
(Q)	1.3	-16	47	99
PTMO-38-3.3 (C)	3.3	-30	47	93
(Q)	3.3	-27	46	102
PTMO-38-6.5 (C)	6.5	-45	43	72
(Q)	6.5	-39	55	81

^A Midpoint (1/2 ΔC_p)

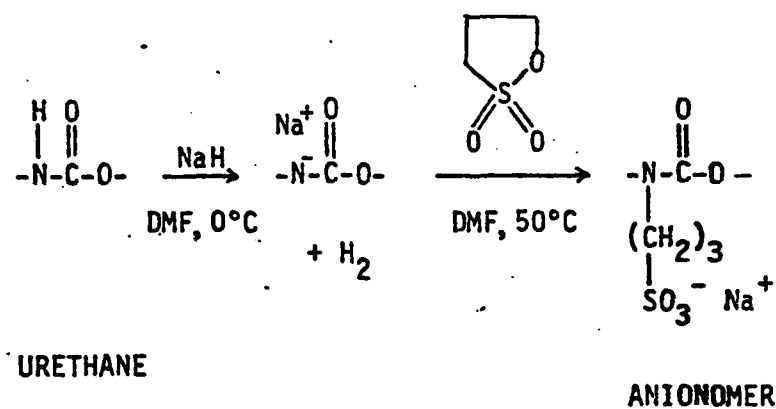
* C = Control
Q = Quench

Table IV
Dynamic Mechanical Data

Sample	β_{\max} (°C)(T _g)	β'_{\max} (°C)	<u>Plateau Zone (°C)</u>		
			Onset	End	Width
PTMO-20	-35	-	-	-	-
PTMO-20-8	-47	-	-10	68	78
PTMO-20-4.5	-50	53	-16	75	91
PTMO-20-10.3	-54	81	-22	155	177
PTMO-20-12.1	-63	100	-26	180	206
PTMO-38	-32	-	0	109	109
PTMO-38-1.3	-21	96	8	87	69
PTMO-38-3.3	-20	95	21	84	63
PTMO-38-6.5	-32	100	-3	95	98

Table V
Stress Strain Properties

<u>Sample</u>	<u>E_y (MPa)</u>	<u>σ_b (MPa)</u>	<u>ϵ_b (%)</u>
PTMO-20	-	-	-
PTMO-20-2.6	0.014	-	300
PTMO-20-6.6	5.4	0.07	1250
PTMO-20-11.1	5.4	10.0	400
PTMO-20-13.2	84	14.0	30
PTMO-38	42	23.0	535
PTMO-38-1.3	49	27	660
PTMO-38-3.3	53	32	580
PTMO-38-6.5	110	27	375



SCHEME 1

FIGURE CAPTIONS

- Figure 1. Effect of ionization on the infrared spectra of PTMO-20 and PTMO-38
- Figure 2. DSC thermograms for the PTMO-20 series of polyurethanes
- Figure 3. DSC thermograms for the PTMO-38 series of polyurethanes
- Figure 4. Effect of ionization on the dynamic mechanical properties of PTMO-20
- Figure 5. Effect of ionization on the dynamic mechanical properties of PTMO-38
- Figure 6. Stress-strain curves for the PTMO-20 series of polyurethanes
- Figure 7. Stress-strain curves for the PTMO-38 series of polyurethanes

PTMO-20

PTMO-20-10.3

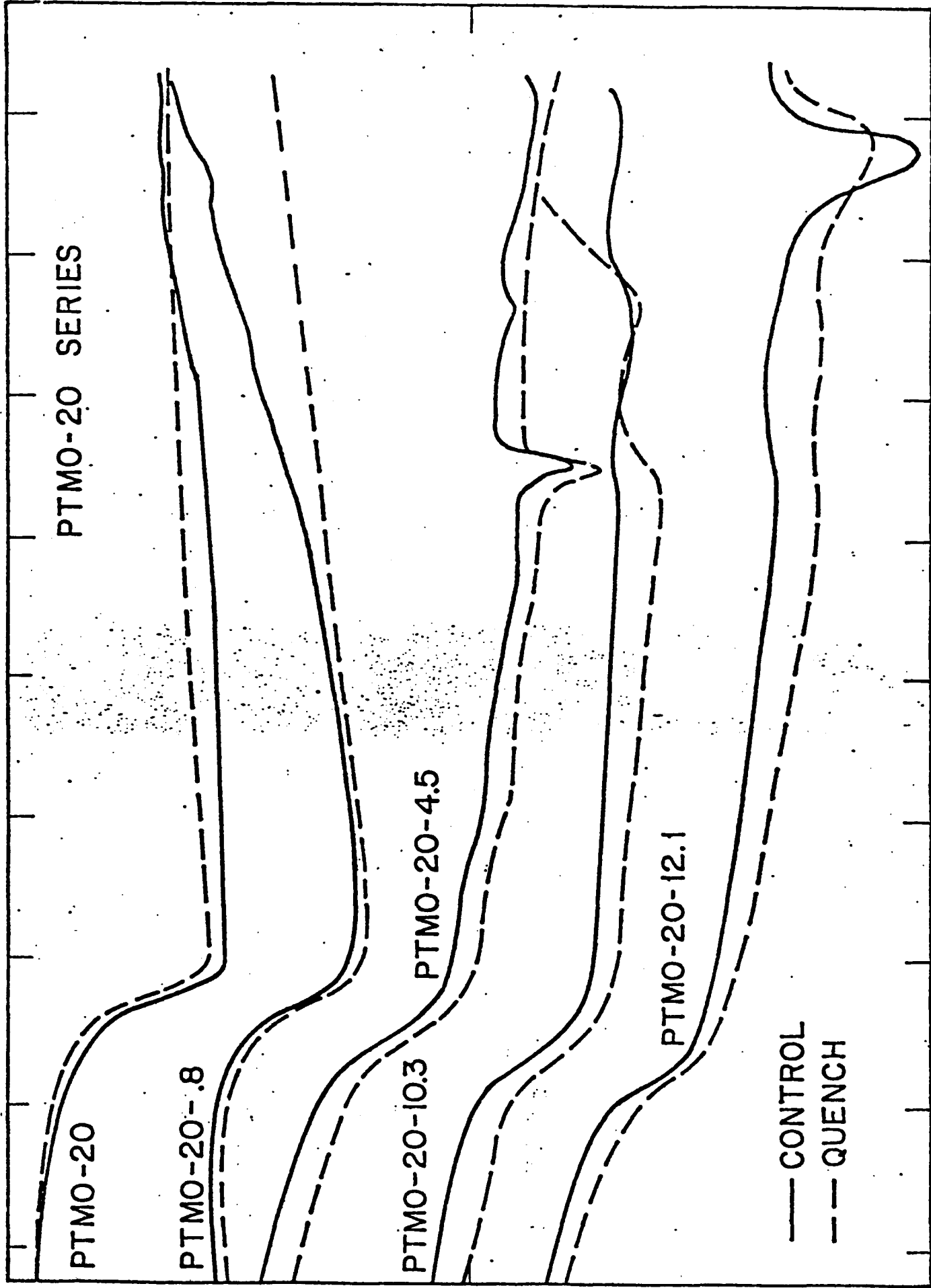
PTMO-38

PTMO-38-6.5

3500 3000 1600 1400 1200 1000 800

WAVE NUMBER (cm^{-1})

FIG 1



-120 -80 -40 0 40 80 120 160 200

↑ ENDO ΔQ

→ ENDO ΔQ

PTMO-38 SERIES

PTMO-38

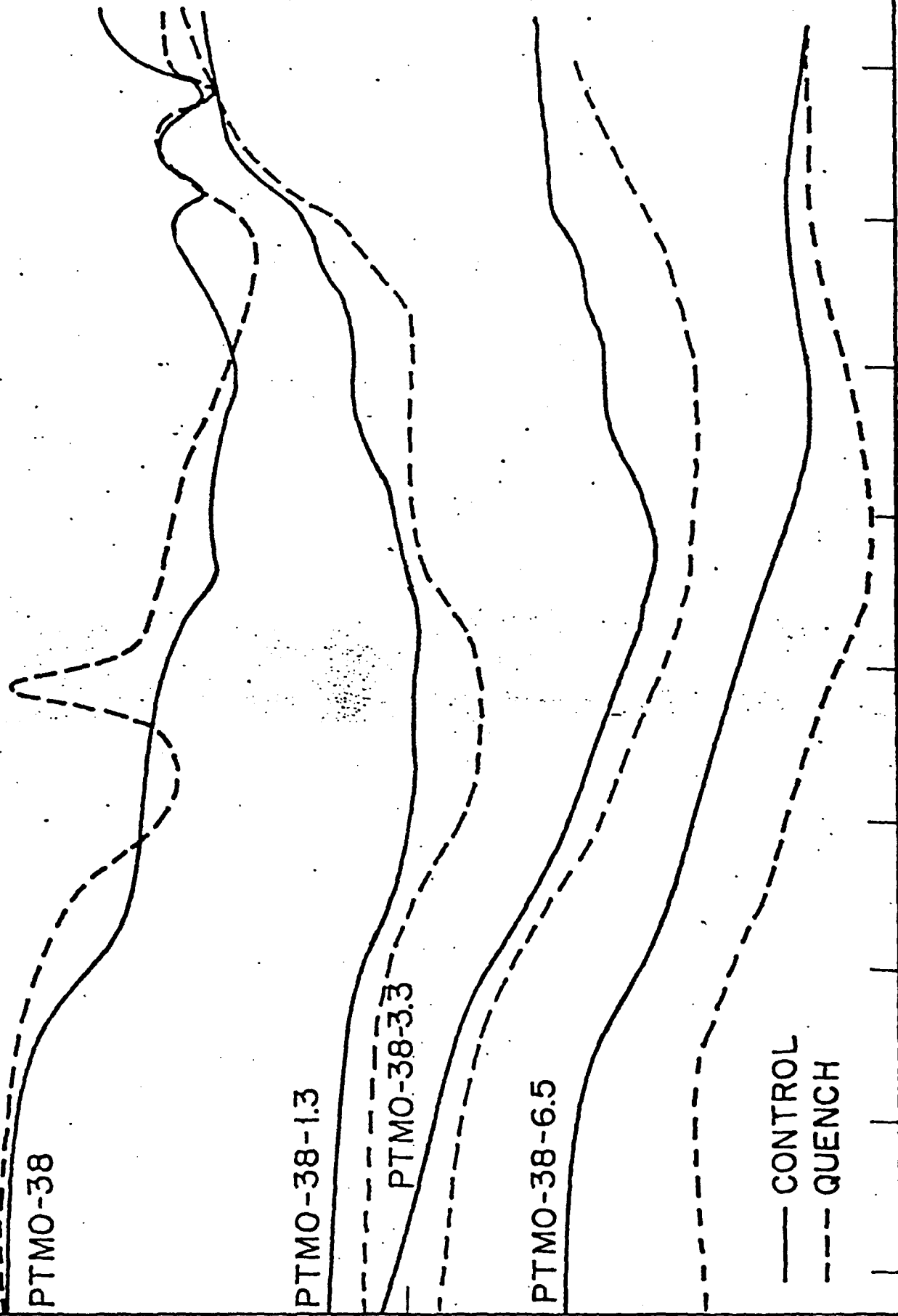
PTMO-38-1.3

PTMO-38-3.3

PTMO-38-6.5

— CONTROL
--- QUENCH

-120 -80 -40 0 40 80 120 160 200



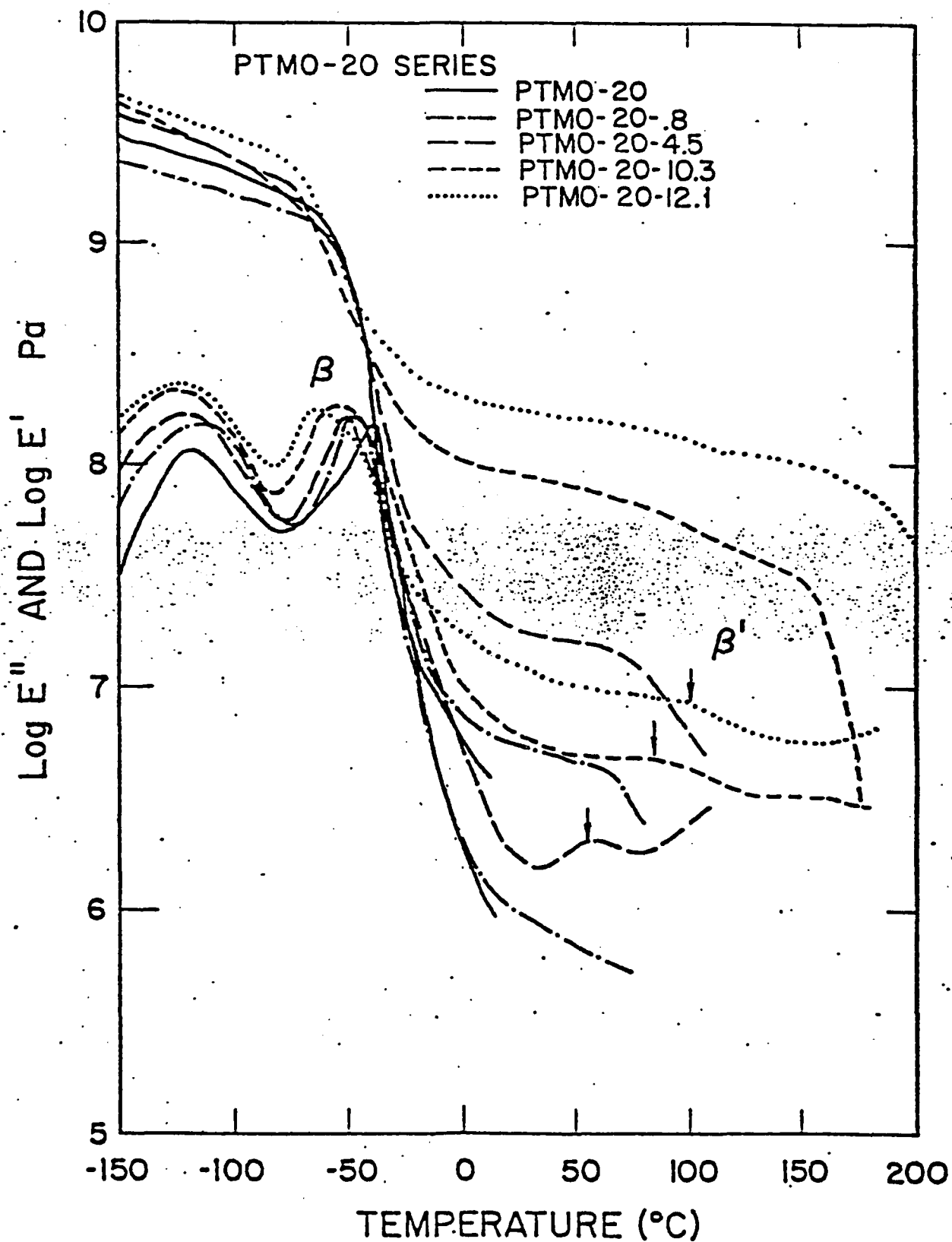


FIG 4

LOG E" AND LOG E' , Pa

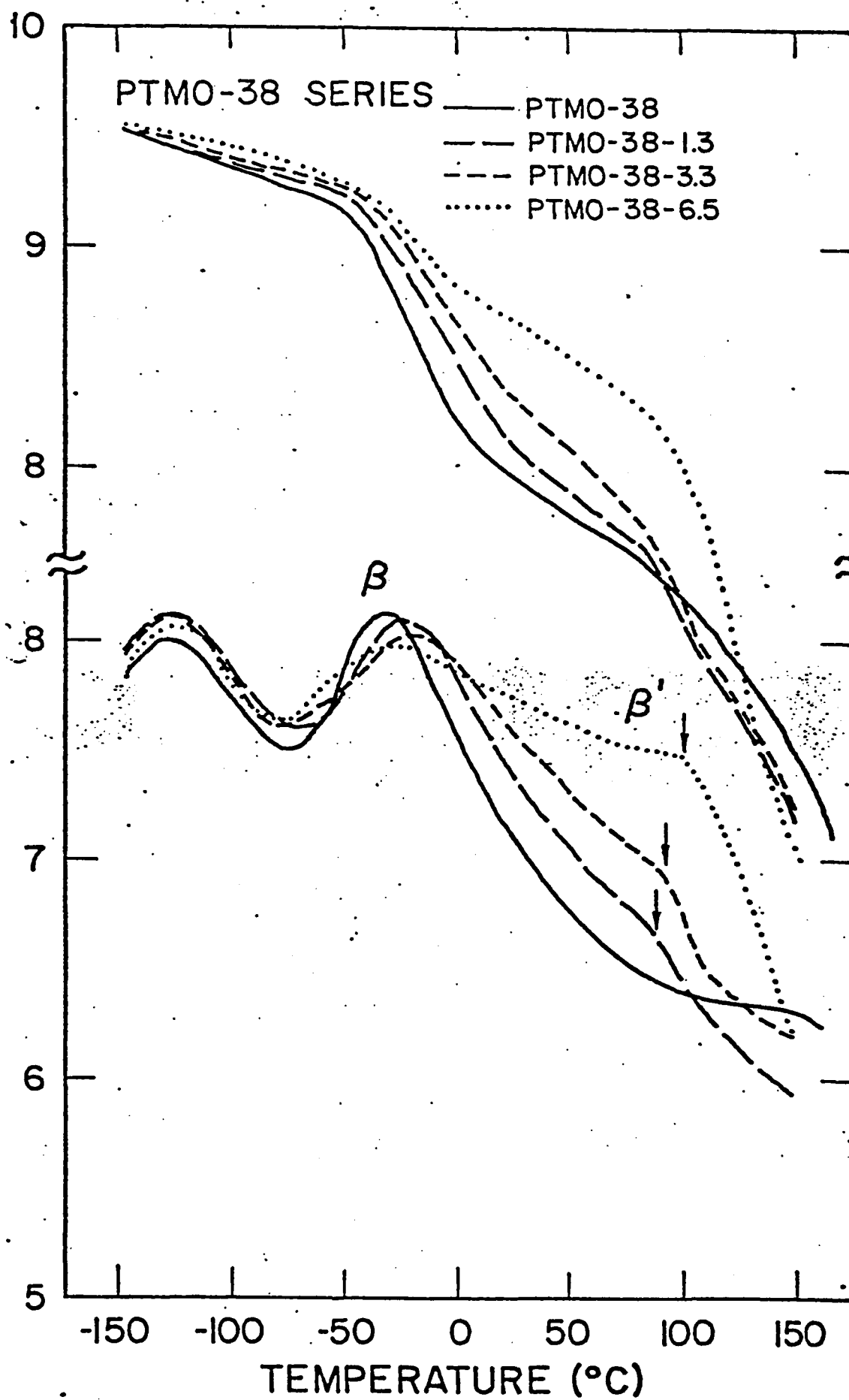


FIG 5

PTMO-20 SERIES

STRESS, MPa

15

PTMO-20-12.1

10

PTMO-20-10.3

5

PTMO-20-4.5

0

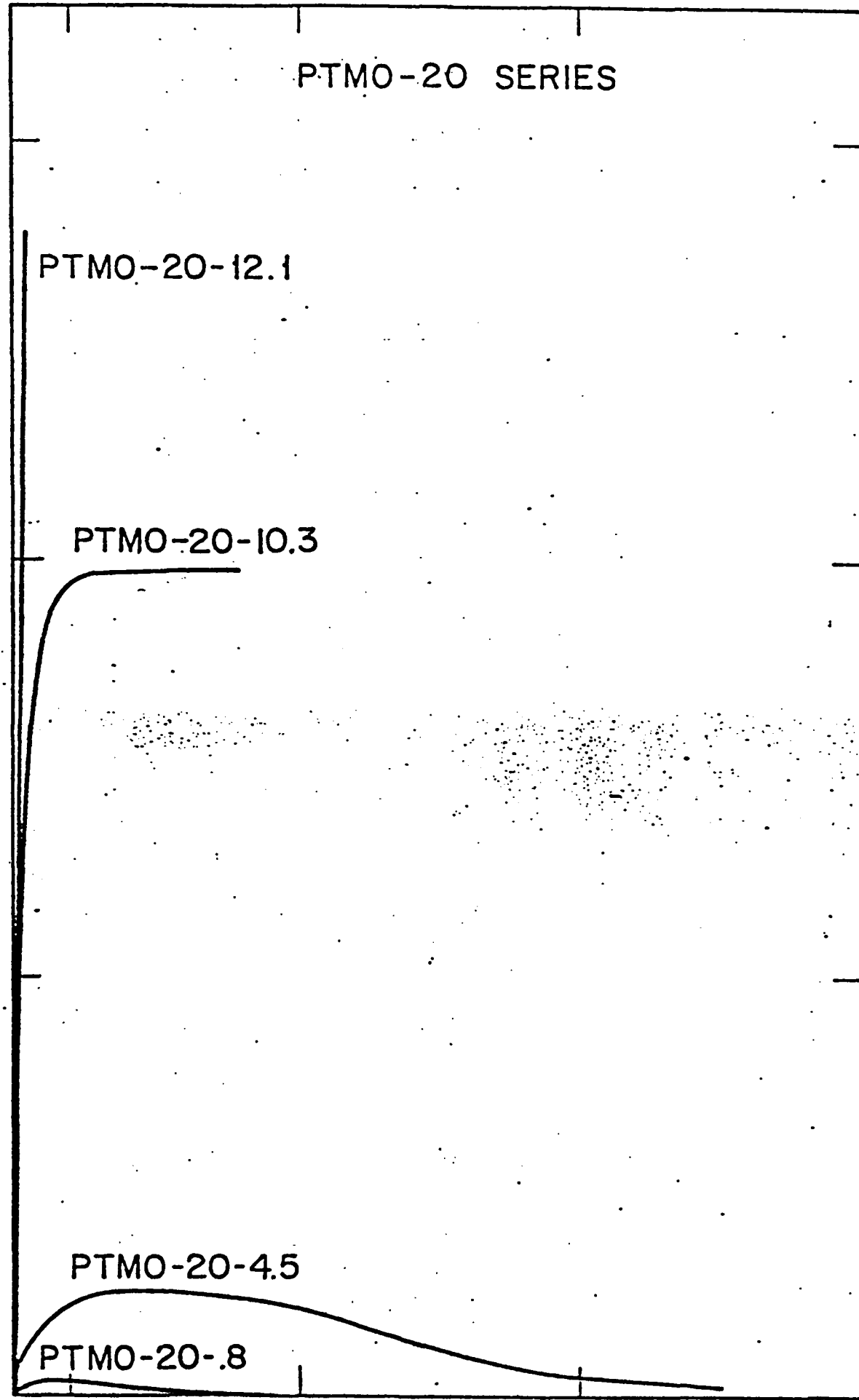
PTMO-20-.8

100

500

1000

1500



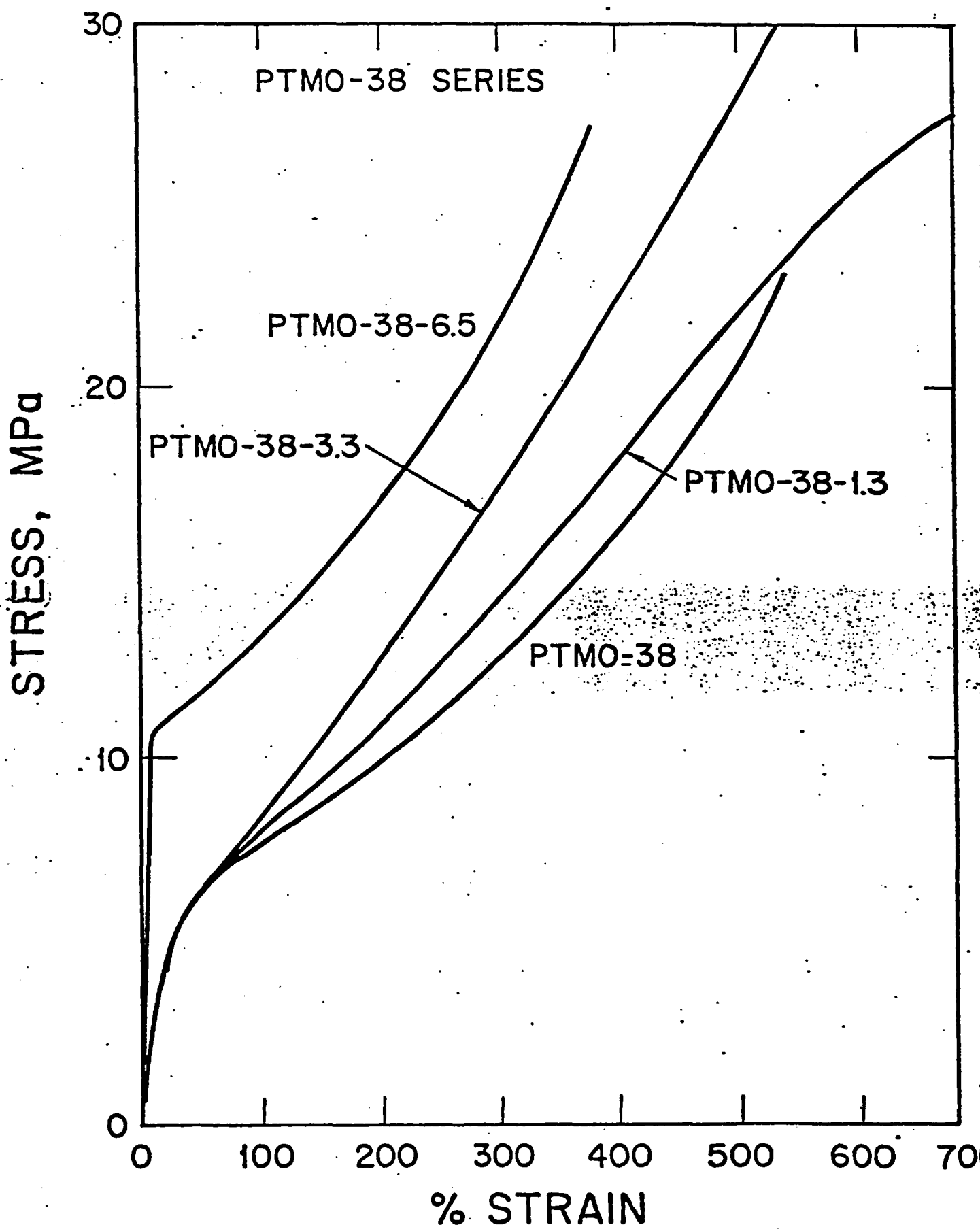


FIG 7

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. Vincent Schaper DTNSRDC Code 2830 Annapolis, Maryland 21402	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

Dr. C. L. Schilling
Union Carbide Corporation
Chemical and Plastics
Tarrytown Technical Center
Tarrytown, New York 10591

Dr. A. G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19174

Dr. E. Fischer, Code 2853
Naval Ship Research and
Development Center
Annapolis, Maryland 21402

Dr. H. Allcock
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Dr. M. Kenney
Department of Chemistry
Case Western University
Cleveland, Ohio 44106

Dr. R. Lenz
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Dr. M. David Curtis
Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48105

NASA-Lewis Research Center
Attn: Dr. T. T. Serafini, MS 49-1
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. J. Griffith
Naval Research Laboratory
Chemistry Section, Code 6120
Washington, D.C. 20375

Professor G. Wnek
Department of Materials Science
and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. R. Soulen
Contract Research Department
Pennwalt Corporation
900 First Avenue
King of Prussia, Pennsylvania 19406

Dr. G. Goodman
Globe-Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201

Dr. Martin H. Kaufman
Code 38506
Naval Weapons Center
China Lake, California 93555

Dr. C. Allen
Department of Chemistry
University of Vermont
Burlington, Vermont 05401

Professor R. Drago
Department of Chemistry
University of Florida
Gainesville, Florida 32611

Dr. D. L. Venezky
Code 6130
Naval Research Laboratory
Washington, D.C. 20375

Professor T. Katz
Department of Chemistry
Columbia University
New York, New York 10027

Professor James Chien
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Professor J. Salamone
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

CAPT J. J. Auburn, USNR
AT&T Bell Laboratories
Room 6F-211
600 Mountain Avenue
Murray Hill, New Jersey 07974

TECHNICAL REPORT DISTRIBUTION LIST, 3568

Professor D. Grubb
Department of Materials Science
and Engineering
Cornell University
Ithaca, New York 14853

Professor T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Professor C. Chung
Department of Materials Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Professor Malcolm B. Polk
Department of Chemistry
Atlanta University
Atlanta, Georgia 30314

Dr. D. B. Cotts
SRI International
333 Ravenswood Avenue
Menlo Park, California 94205

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Avenue
Azusa, California 91702

Professor H. Hall
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Professor G. Whitesides
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Professor H. Ishida
Department of Macromolecular Science
Case Western University
Cleveland, Ohio 44106

Dr. K. Paciorek
Ultrasystems, Inc.
P.O. Box 19605
Irvine, California 92715

Professor D. Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. G. Bryan Street
IBM Research Laboratory, K32/281
San Jose, California 95193

